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## On the use of benzaldehyde to improve the storage stability of one-pot, epoxy ionic liquid formulations.

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**ABSTRACT:** A series of adducts were prepared based on the reaction of 1-ethyl-3-methylimidazolium acetate and benzaldehyde in various stoichiometries (from equimolar reaction to benzaldehyde in 10-fold excess) and the resulting adducts were characterized using nuclear magnetic resonance spectroscopy (<sup>1</sup>H, <sup>13</sup>C, DEPT, and HQSC experiments). Differential scanning calorimetry was used to examine the initiating behaviour of the adducts towards mono- and di-functional epoxy resins and the data were used to determine kinetic parameters for the polymerization. The lower temperature peak, due to carbene formation, is sensitive to adduct concentration; the residual ionic liquid in the adduct mixture contributes towards the initiation of the curing reaction. When a monofunctional epoxy and the 1:1 adduct was subjected to a 2-week period of storage at room temperature and sub-zero temperatures in the freezer, the profiles of the thermograms for the frozen samples do not change considerably over the storage period and the formulation retains a light yellow colour (rather than the viscous, dark red appearance of the formulation stored at room temperature).

**Keywords:** Epoxy Resins, Ionic Liquids, Initiators, Latent Cure.

## INTRODUCTION

Imidazoles have proven to be very effective initiators of the polymerization of epoxy resins [1,2], and yield adhesives and coatings with very good thermal, mechanical, and electrical properties [3,4,5]. They are also used as anticorrosive coatings, adhesives, and paints due to their corrosion resistance and good adhesion to a wide variety of substrates [6,7]. Studies have also shown that epoxy resins cured with imidazoles can have superior physical properties [8] such as better heat resistance [9], lower tensile elongation, a higher modulus, and a wider range of cure temperatures compared with amine-cured systems [10,11]. It is for this reason that such materials are added to commercial epoxy resins to catalyse the homopolymerisation of epoxide groups and yield tough thermoset networks. Previous research has shown a dependence of reaction rate and conversion on the oligomeric length of the epoxy. Fernández-Franco *et al.* reported that 2 parts per hundred parts resin (phr) of 1-methylimidazole was not sufficient to completely cure a DGEBA oligomer with a molecular weight of 364 g/mol [12], but Ooi *et al.* reported complete cure with an DGEBA oligomer with MW = 381 g/mol [13], when examining the differences in curing behaviour observed for three structurally-related imidazoles (containing 1-methyl-, 2-methyl-, and 2-phenyl-substituents) of steric *versus* inductive effects. It has been found that as the molecular weight of the DGEBA oligomer is raised, the reaction rate and the degree of conversion achieved both increase leading the researchers to conclude that the hydroxyl content in the DGEBA oligomer plays a major role on the reaction rate and also the conversion<sup>a</sup>. One of the main drawbacks to the use of imidazoles is their poor shelf life in the one pot formulations, allowing polymerization to proceed during storage, and various researchers have employed the use of complexing agents to coordinate the lone pair of electrons on the unsubstituted nitrogen atom in the imidazole ring [14].

Increasingly, researchers have turned to structurally related imidazolium-based ionic liquids [15], which are often selected due to the stability of the ring in oxidative and reductive environments, the low viscosity exhibited and the relative ease of synthesis [16]. However, whilst various research groups have championed the use of imidazolium-based ionic liquids as catalysts for enhancing both the rate of reaction and the yield [17], to date only a few studies in the literature report imidazolium-based ionic liquids as initiators for epoxy resins. For example, Kowalczyk and Szychaj [18] reported that 1-butyl-3-methylimidazolium tetrafluoroborate could be used as an initiator for a commercial epoxy (Epidian 6) and that a formulation comprising the two components could be stored for a period of 6 months at ambient temperature without any change in viscosity. Rahmathullah *et al.* [19] found that 1-ethyl-3-methylimidazolium dicyanamide could be used as a latent initiator for a commercial bisphenol A based epoxy (Epon 828, DGEBA); remaining miscible

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<sup>a</sup> For reference, in the present work, the study was carried out on a commercial epoxy with EEW 182 g/mol.

and exhibiting long-term stability at room temperature. The stability of the formulation was tracked through monitoring the characteristic epoxy ring absorbance band in near-infrared (NIR) spectroscopy and it was suggested by the authors that the mechanistic route might involve reaction between the cyanamide and epoxy groups and not the nitrogen atoms in the imidazolium cation directly. Maka *et al.* [20] reported the use of imidazolium-based ionic liquids based on both 1-decyl-3-methylimidazolium and 1-butyl-3-methylimidazolium cations with chloride, tetrafluoroborate and dicyanamide anions as initiators for epoxy resins. It was suggested that thermal decomposition of the ionic liquid could proceed *via* a highly stabilised *N*-heterocyclic carbon structure that, in turn, would result in generation of imidazole or 1-alkyl derivatives. The interaction of the pyridine-type nitrogen atom in the imidazole ring with an epoxy group to form a 1:1 adduct was concluded as the most likely anionic polymerisation route.

Several authors have suggested that thermal decomposition of 1,3-dialkylimidazolium-based ionic liquids yields imidazole and alkylimidazole derivatives that are capable of initiating epoxy resins to undergo anionic polymerisation. The reported ease of carbene formation from certain ionic liquids raises questions with respect to the mechanistic pathway and whether the mechanism is generally applicable to imidazolium-based ionic liquids. The current work seeks to develop a novel, one-pot epoxy-ionic liquid formulation, capable of long-term storage without detriment to its initiating capability.

## EXPERIMENTAL

### Materials.

1-Ethyl-3-methylimidazolium acetate (IL), 1-ethyl-3-methylimidazolium thiocyanate, and the diglycidyl ether of bisphenol A (DGEBA, Baxxores<sup>TM</sup> ER 2200,  $M_w$  182 g/mole) were supplied by BASF, and phenylglycidylether (PGE, 99 %) was purchased from Sigma Aldrich (now Merck). The materials were characterised using <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy and used without further purification (see supplementary data, Fig. S1 and S2).

### Instrumentation.

<sup>1</sup>H NMR spectra comprising 16 scans and <sup>13</sup>C NMR spectra (100 scans) were conducted on a Bruker 300 MHz NMR spectrometer at 298 K. The samples for analysis (80 mg) were mixed with D<sub>6</sub>-DMSO (0.6 – 0.7 ml) and transferred to a NMR tube. For the HSQC experiment, a carbon spectrum was obtained which consisted of 200 scans in order to improve the resolution for analysing the coupling between the carbon atoms and protons. A COSY spectrum consisted of two scans. Data were processed using TopSpin 3.0 produced by Bruker BioSpin.

Infra-red spectra were obtained (32 scans between 4000-600  $\text{cm}^{-1}$ ) using an Agilent Technologies Cary 600 Series Fourier Transform Infrared spectrometer employing a golden gate accessory with a diamond crystal (ATR-IR spectroscopy). A background spectrum consisting of 32 scans with the golden gate *in situ* was run before all analyses. The resulting spectrum for each sample was taken from an average of 32 scans which were recorded in absorbance mode over a spectral range of 600 – 4000  $\text{cm}^{-1}$ . The samples were placed directly on the sapphire platform and good contact between the diamond crystal and sample was checked prior to commencement of analysis. The data were processed using Agilent Resolutions Pro.

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q1000 running TA Q Series Advantage software on samples ( $5.0 \pm 0.5$  mg) in hermetically sealed aluminium pans. Experiments were conducted at a heating rate of 10 K/min. from -10 °C to 400 °C (heat/cool/heat) under flowing nitrogen (50  $\text{cm}^3/\text{min.}$ ). DGEBA and ionic liquid were combined in a glass scintillation vial and mixed by hand. The samples were immediately analysed after mixing and the remaining mixture placed in the freezer.

Dynamic oscillatory rheology was performed using an Anton Paar MCR-300 rheometer with a 25 mm peltier plate and disposable aluminium pan set up. The rheometer was operated in oscillation mode and samples were subjected to a temperature ramp from 25 °C to 200 °C at 5 K/minute with the collection of data set to a frequency of 0.2 minutes. The strain was held constant at 0.5 % and the normal force programmed to remain at 0 N. DGEBA and ionic liquid were combined in a speed mixer pot (100 g) and subjected to two consecutive mixing periods of two minutes at 2000 rpm.

Dynamic mechanical thermal analysis (DMTA) data were acquired with a TA Instruments DMA Q800 using a single cantilever clamp requiring sample dimensions of 17.5 mm (L) and up to 15 mm (W) and 5 mm (T). The instrument was programmed to perform a temperature ramp from ambient temperature to 230 °C at 5 K/min at a constant strain of 0.1% and a single frequency of 1 Hz. The tan delta sensitivity and the modulus precision are reported to be 0.0001 and  $\pm 1\%$  respectively according to the instrument specification and the data were processed using Universal Analysis 2000 from TA Instruments.

Gelation measurements were measured using a GELNORM®-RVN Topfzeitmessgeräts instrument operating according to DIN 16945 [21], which defines the pot life as the point at which the sample exhibits a 5% increase in viscosity compared with the starting value. This is calculated by measuring the relative viscosity through the change in power required over time for a spindle probe inserted in the sample to rotate. An aluminum stamper was inserted into the test tube and subsequently affixed to the moving lever within the instrument. The test tube was placed in the furnace and the Ni-Cr-Ni thermocouple placed inside the reacting mixture. The instrument was

programmed to heat the furnace to a specified temperature and then begin moving the aluminium stamper up and down. The gel time was recorded at the point at which the test tube was lifted out of the furnace by the stamper (due to an increase in the viscosity) causing the optical line of light to be broken. The DGEBA and ionic liquid were combined in a glass beaker (100 ml) and mixed by hand for 120 seconds. A sample (*ca.* 12 g) was subsequently transferred to a glass test tube for analysis.

**Preparation of adducts.** The direct reaction of 1-ethyl-3-methylimidazolium acetate and benzaldehyde was adapted from the work by Rogers *et al.* [22] and was carried out using the masses presented in Table 1. The amount of benzaldehyde was kept constant while the amount of 1-ethyl-3-methylimidazolium acetate was varied accordingly to produce the different adducts. The required amounts of benzaldehyde and 1-ethyl-3-methylimidazolium acetate were weighed into a glass scintillation vial and a magnetic stirrer bar was added. The mixtures were stirred for approximately 15 minutes at room temperature or until a noticeable change in viscosity was observed.<sup>b</sup> A second method was employed in which the adduct was not isolated, but rather the components of the formulation: benzaldehyde (0.16 g), 1-ethyl-3-methylimidazolium acetate (0.25 g), and DGEBA (5 g) were mixed simultaneously and then analysed immediately.

Table 1. Mixing weights for preparation of adducts comprising 1-ethyl-3-methylimidazolium acetate (IL) and benzaldehyde (B).

Molar ratio (IL:B)	1-Ethyl-3-methylimidazolium acetate, IL (g)	Benzaldehyde, B (g)
1:1	2.622	1.637
0.7:1	1.787	1.637
0.5:1	1.277	1.637
0.1:1	0.255	1.637

<sup>b</sup> The same reaction conditions were employed with an equimolar mixture of 1-ethyl-3-methylimidazolium thiocyanate (2.611 g) and benzaldehyde (1.637 g), but the resulting <sup>1</sup>H NMR spectrum revealed no new peaks relating to adduct formation. This suggests that the thiocyanate anion is not sufficiently basic to promote deprotonation of the cation and subsequent reaction with benzaldehyde at room temperature in the absence of an additional base.

***Storage studies comprising PGE and 1-ethyl-3-methylimidazolium acetate-benzaldehyde adduct.***

The materials were weighed into clear glass scintillation vials and analysed using DSC immediately after mixing. The masses of both components used in the formulations are shown in Table 2 (the number of moles of 1-ethyl-3-methylimidazolium acetate was kept consistent to allow comparison between the final results).

Table 2. Mixing weights for formulations comprising PGE, 1-ethyl-3-methylimidazolium acetate, and the 1-ethyl-3-methylimidazolium acetate-benzaldehyde adduct (IL-B).

1-Ethyl-3-methylimidazolium acetate, IL (g)	IL-B (g)	PGE (g)
1:1	0.41	5.00
0.7:1	0.47	5.00
0.5:1	0.56	5.00

Subsequently, samples of each formulation were stored at both room temperature and in the freezer for further analysis; a 30-minute period out of the freezer was allowed to elapse before measurement. All samples (0.8 mg) were subjected to a heat-cool-heat temperature programme from 20 °C to 190 °C at 10 K/min under nitrogen.

## **RESULTS AND DISCUSSION**

Our previous publications [23,24] highlighted the importance of the acidic hydrogen atom and the role of the anion in combination with the cation when employed as initiators for the polymerisation of epoxies. Several different reaction pathways have been proposed for the initiation reaction with a di-epoxy is proposed to occur *via* a carbene route, an imidazole route or a nucleophilic route (Fig. 1), although it is suggested that these reaction pathways are not discrete.

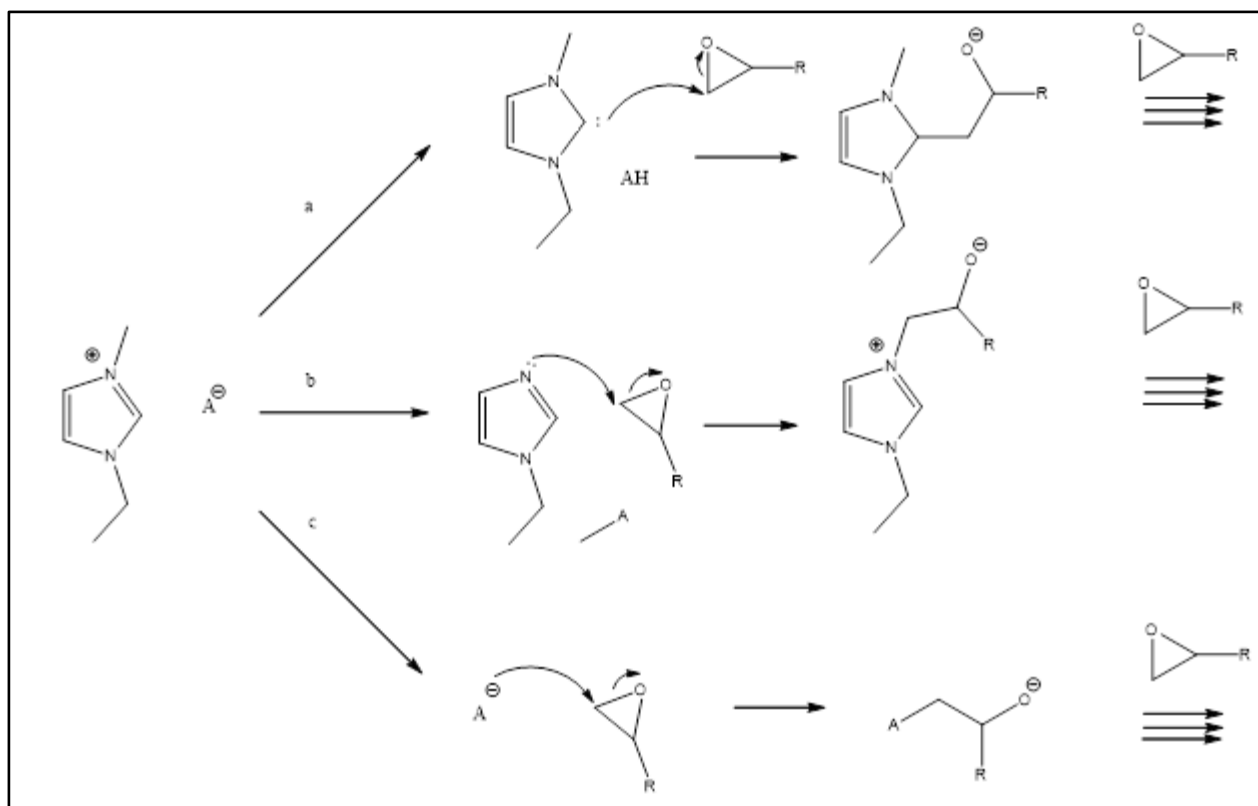
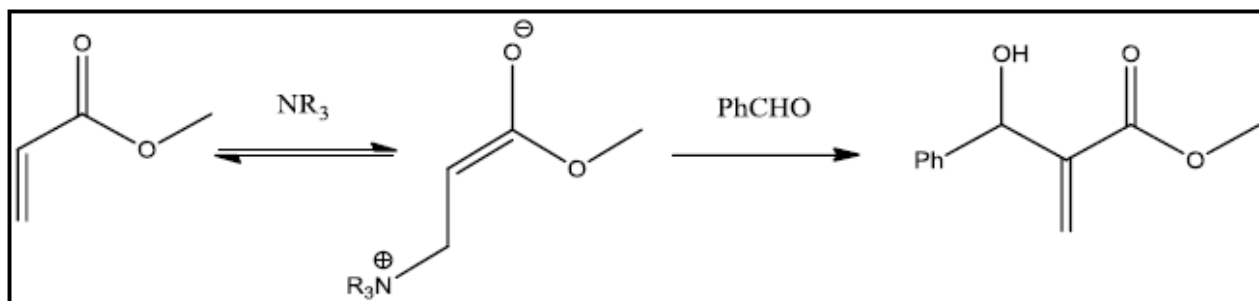


Figure 1. Proposed reaction pathways for initiation of an epoxy polymerization reaction with imidazolium-based ionic liquids *via* a) the ‘carbene route’, b) the ‘imidazole route’ and c) the ‘counter ion’ route.

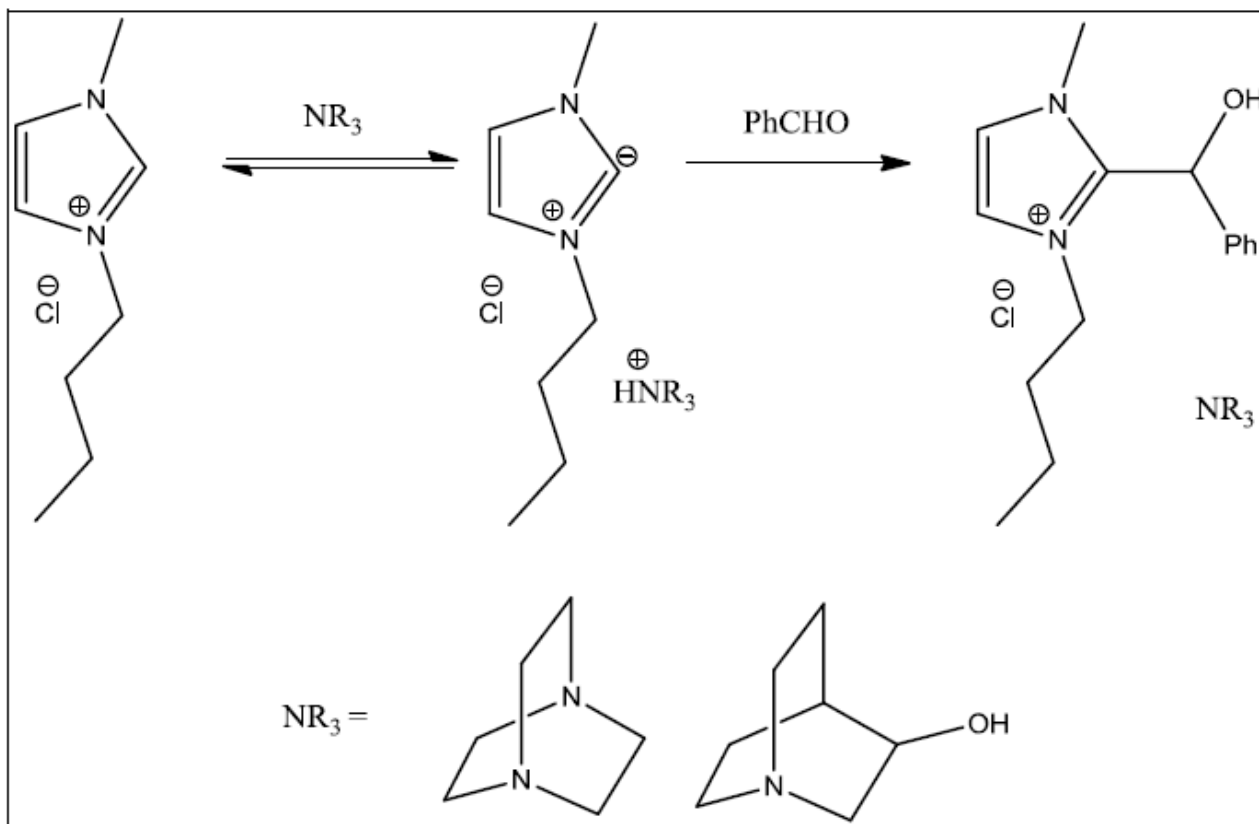
A methyl group, substituted in place of the acidic hydrogen atom, is observed to undergo deuterium exchange in the presence of a weak base [25] and thus, it was necessary to employ a more complex group which reacts with the ionic liquid at the acidic position. It was envisaged that such a compound would react with the ionic liquid, in the absence of a solvent, and form an adduct-type structure which would improve the latency of the formulation whilst, itself, being non-initiating towards the epoxy monomer. While studying the influence of protecting groups on the diastereoselectivity of catalytic heterogeneous hydrogenation of Baylis-Hillman adducts (Scheme 1a), Rosa and Afonso [26] reported an enhanced reaction rate with the addition of the ionic liquid.

(a)





(b)



Scheme 1 (a) The Baylis-Hillman reaction ( $\text{NR}_3$  = 3-hydroxy quinuclidine) and (b) reaction between 1-butyl-3-methylimidazolium chloride and benzaldehyde.

A subsequent study by Aggarwal *et al.* [27] revealed that a significant side reaction was occurring between the benzaldehyde (the aldehyde component in the Baylis-Hillman reaction) and the ionic liquid. While Rosa and Afonso had used gas chromatography to monitor the rate of formation of the product with respect to benzaldehyde only, Aggarwal *et al.* concluded that, whilst the disappearance of benzaldehyde was faster in the presence of the ionic liquid, the rate at which it was converted did not match the rate at which the methyl acrylate was consumed. This in turn suggested that the faster consumption of benzaldehyde in the presence of ionic liquid was actually due to the ionic liquid, under the mildly basic conditions of the reaction, being deprotonated and reacting with benzaldehyde as shown

in Scheme 1 (b). Consequently it was decided to replicate the work of these authors, by employing molar ratios of 1:1, 0.7:1, 0.5:1 and 0.1:1 (ionic liquid:benzaldehyde), and replacing the neat ionic liquid in the epoxy formulation with the adduct to observe whether this affected the latency of the formulation by impacting the proposed reaction mechanism involving carbene formation.

*Characterisation of adducts comprising 1-ethyl-3-methylimidazolium acetate (IL) and benzaldehyde (B).* Following the reaction, the contents of the vessel were examined using  $^1\text{H}$  NMR spectroscopy. The spectra corresponding to the starting materials (benzaldehyde and the ionic liquid) are presented in Fig. 2 along with the shifts assignments in the expansion. The assignments are as expected: for benzaldehyde the aldehydic proton resonates at 10.0 ppm, while expansion of the multiplet (integral 5H) in the region 7.5 – 8.0 ppm shows three distinct peaks consisting of a doublet for the protons situated in the *ortho* position relative to the carbonyl group on the benzene ring, a triplet for the *para* proton and a triplet for the *meta* protons. The doublet representing the *ortho* protons undergoes some additional splitting as a result of long-range coupling with the *para* proton and the carbonyl group which, due to its anisotropic nature, causes splitting of an asymmetric nature. A similar phenomenon exists for the *meta* protons which are shown to undergo some additional asymmetric splitting. The triplet for the *para* proton appears to be much better defined with the further splitting arising from symmetrical long-range coupling between the *ortho* protons, again with the asymmetry from the effect of the carbonyl group [28].

The formation of the adduct leads to the presence of new chemical shifts, which are denoted by ('), while the presence of starting materials is still observed, particularly in the stoichiometric formulation. The aromatic ring protons in the IL-B adduct are also seen to experience an upfield shift. If the 0.1:1 sample is considered, where the benzaldehyde is present in excess, it would be expected that the peaks observed are due principally to the adduct rather than the residual ionic liquid starting material. The corresponding  $^{13}\text{C}$  NMR spectra are presented in Fig. 3. It can be seen that the expected peaks are present from the starting materials with additional peaks which are attributed to changes in the aromatic ring environment upon formation of the adduct; a new peak is observed at approximately 65.0 ppm. A structure for the adduct was postulated (Fig. 3, expansion), and additional NMR spectroscopy was performed on a sample of the 0.5:1 adduct. The HSQC spectrum (Fig. 4) revealed the coupling of the protons with the carbon atoms. The aromatic ring protons are seen to couple with the aromatic ring carbon atoms (Table 3) and an expansion of the multiplet region, reveals the coupling of the new proton environments to the carbon atoms in the new environment. The new peak in the  $^1\text{H}$  NMR spectrum is shown to couple with the new carbon environment in the  $^{13}\text{C}$  NMR spectrum and is consistent with a CHOH moiety.

Table 3. Summary of coupling of carbon atoms and protons in the 0.5:1 IL-B adduct obtained from an HSQC NMR spectrum

Proton	Carbon
11	E
8, 2, 3, 10, 9	D, B, A, C, 2, 3
8', 2', 3', 10', 9'	D', B', C', A'
*	**
4	4
1	1
7	7,8
5	5,4

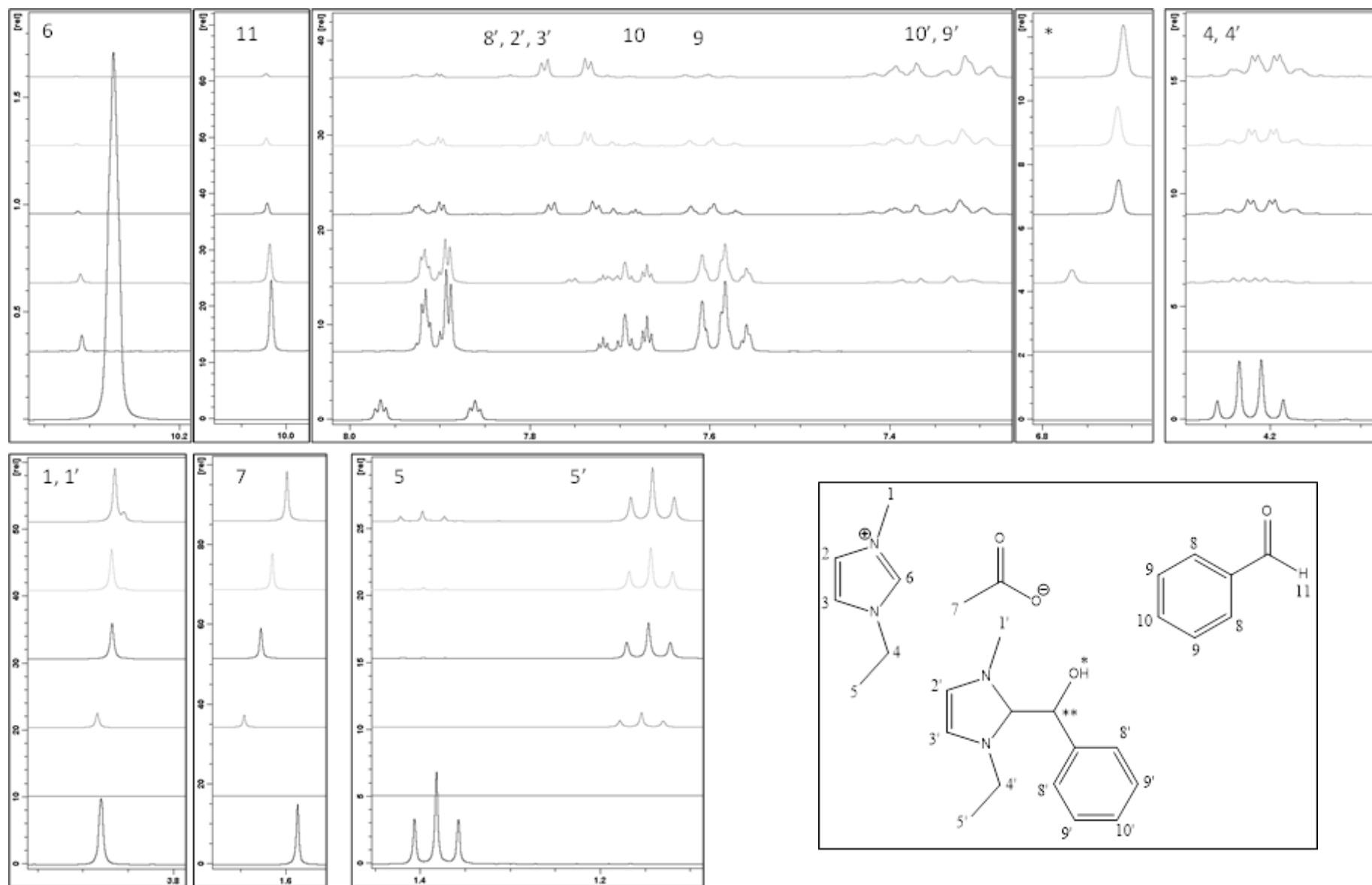


Figure 2 Expanded  $^1\text{H}$  NMR spectra of formulations comprising benzaldehyde and 1-ethyl-3-methylimidazolium acetate in  $\text{D}_6\text{-DMSO}$ .

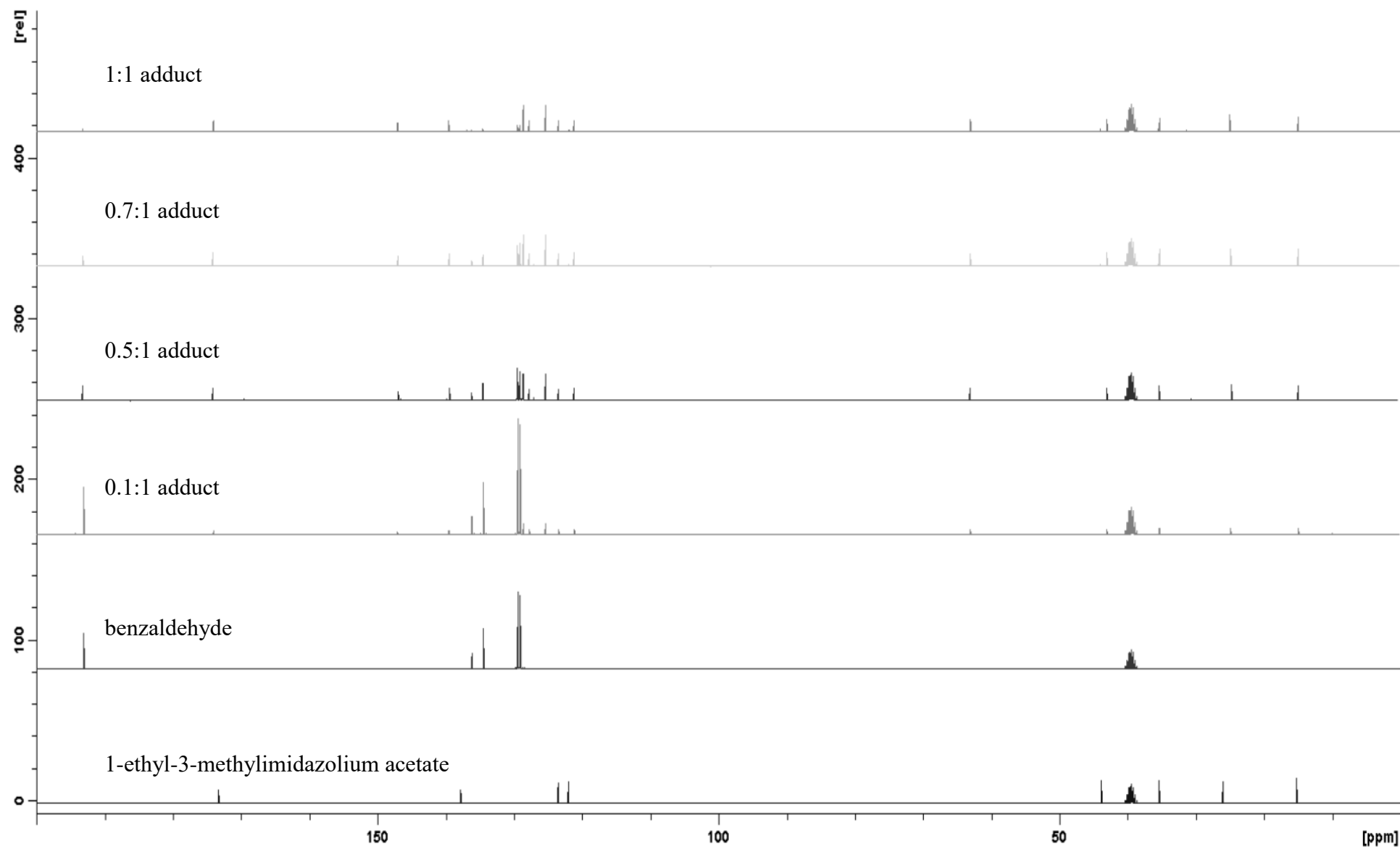


Figure 3 Overlaid  $^{13}\text{C}$  NMR spectra of formulations comprising benzaldehyde (1.637 g) and 1-ethyl-3-methylimidazolium acetate in  $\text{D}_6\text{-MSO}$ .

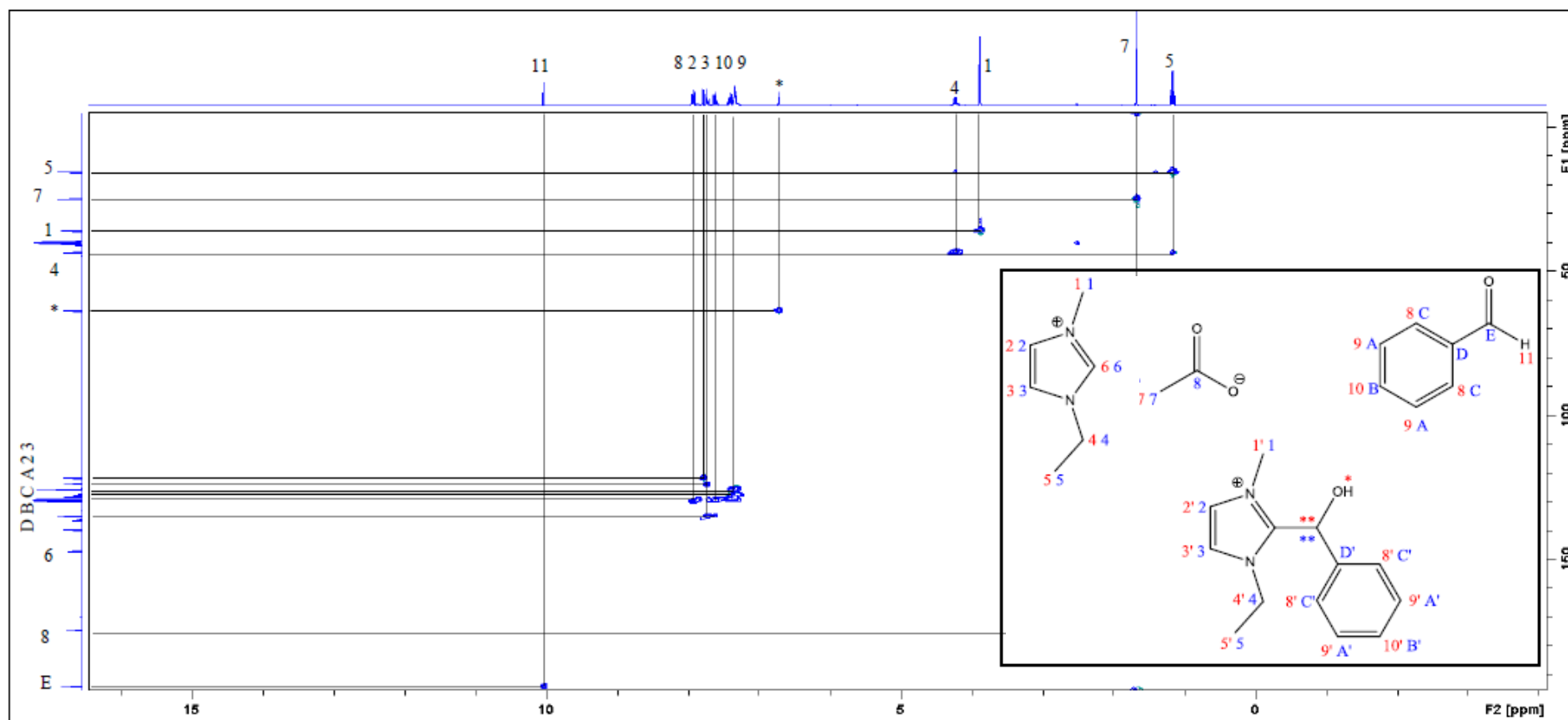


Figure 4 HSQC NMR spectrum of 0.5:1 1-ethyl-3-methylimidazolium acetate-benzaldehyde adduct in D<sub>6</sub>-DMSO (inset structure: C and H)

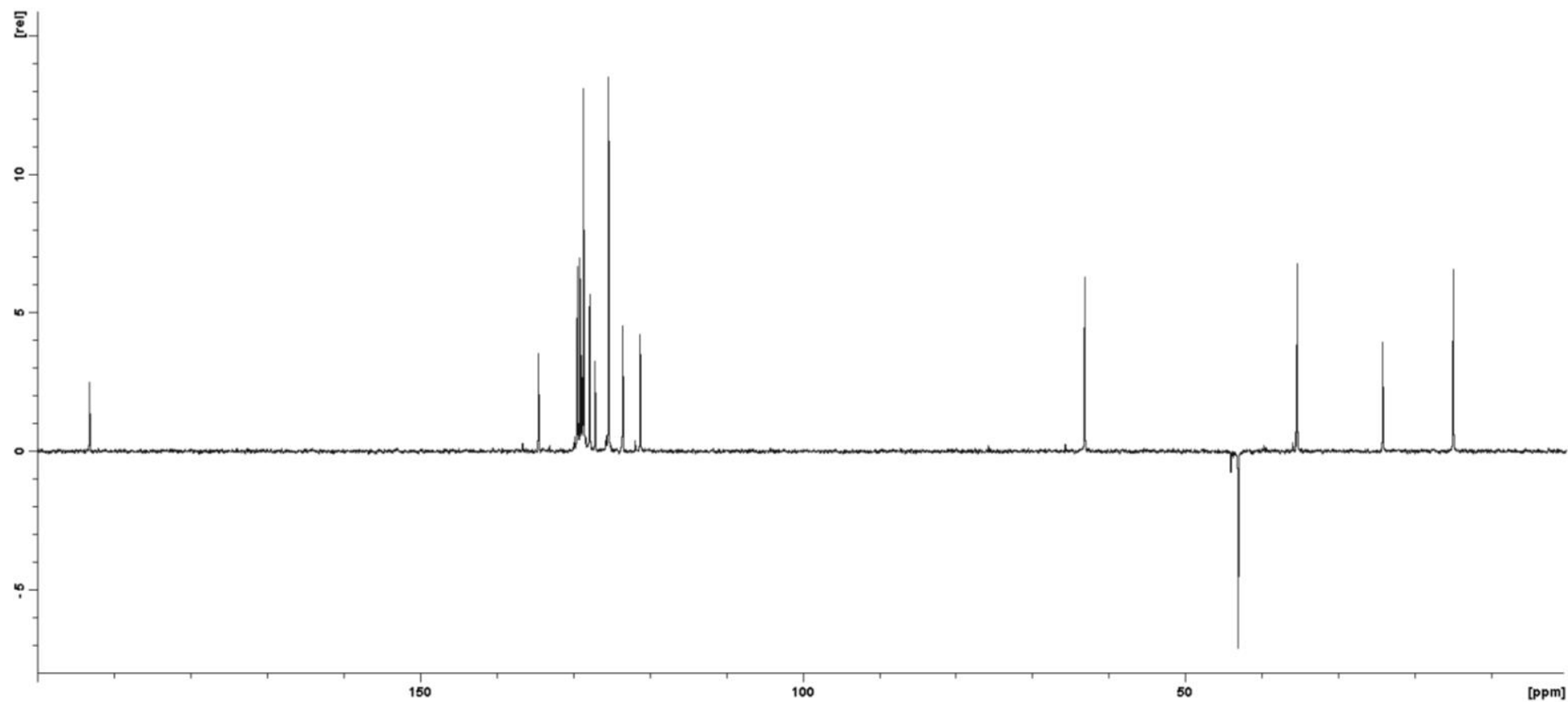


Figure 5 DEPT NMR spectrum of 0.5:1 1-ethyl-3-methylimidazolium acetate-benzaldehyde adduct in D<sub>6</sub>-DMSO



In addition, a DEPT NMR analysis (Fig. 5) confirmed that the new carbon peak was attributable to either a CH or CH<sub>3</sub> environment; all remaining peaks were accounted for in the spectrum (H8 is not seen as it is a quaternary carbon atom). Thus, the NMR data were consistent with the proposed structure. In order to gauge the reaction yield, <sup>1</sup>H NMR was employed to determine the % composition of the IL-B adduct produced (and the residual benzaldehyde), based on the ratio of the peak labelled 11 *versus* the new peak labelled as \*. The percentage conversion of benzaldehyde (PhCHO) to the product (PhCHOH) is presented in Table 4. It can be seen that as the amount of ionic liquid increases, the percentage of adduct increases and the percentage of unreacted benzaldehyde remaining in the sample decreases.

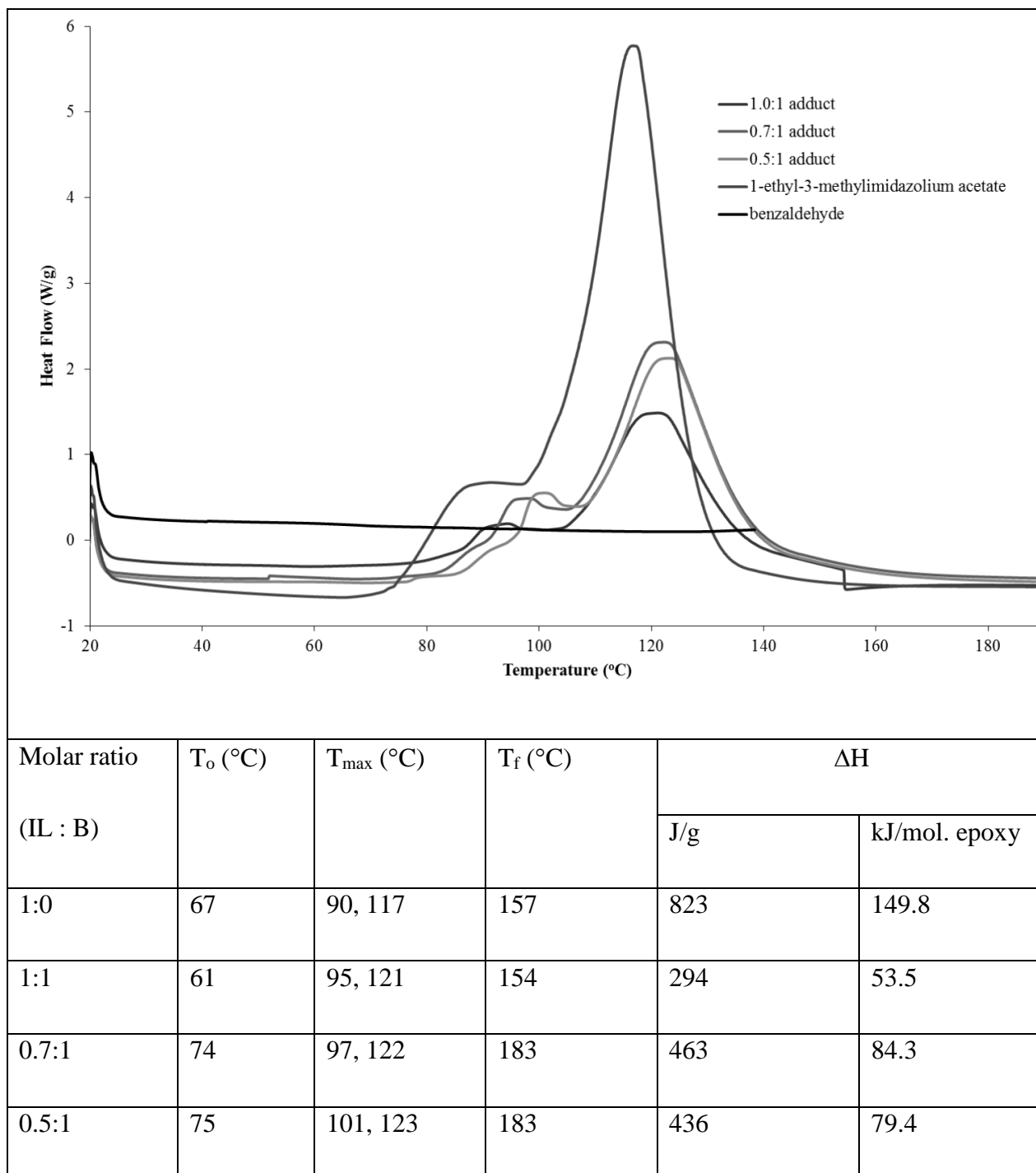
Table 4. Composition of 1-ethyl-3-methylimidazolium acetate-benzaldehyde reaction mixture determined by <sup>1</sup>H NMR spectroscopy

Molar ratio	% Adduct	% Benzaldehyde
0.1:1	10	90
0.5:1	56	44
0.7:1	68	32
1:1	86	14

### Examining the initiation behaviour of the adduct towards epoxy polymerisation

*Influence of the adduct composition.* A comparison of the DSC thermograms resulting from reaction of a monofunctional epoxy (PGE) with the adducts, neat 1-ethyl-3-methylimidazolium acetate, and neat benzaldehyde is presented (Table 5), in each case the main exotherm (representing the polyetherification reaction) is preceded by at least one smaller low temperature event, associated with the initiation reaction. When the PGE is reacted with 1-ethyl-3-methylimidazolium acetate the ionic liquid promotes the polyetherification reaction to produce a linear polymer and an enthalpy of 823 J/g (149.3 kJ/mol. of epoxy group) is recorded. The enthalpy decreases when adducts are employed and, additionally, no reaction is observed when the PGE is heated with benzaldehyde. This lack of an exothermic peak in the benzaldehyde/PGE sample implies that the change in profile between the 1-ethyl-3-methylimidazolium acetate/PGE samples and the adduct/PGE samples is due to the varying amount of free 1-ethyl-3-methylimidazolium acetate present.

Table 5. Dynamic DSC data (heat 1) for freshly mixed formulations comprising PGE (5 g) and 1-ethyl-3-methylimidazolium acetate-benzaldehyde adduct as a function of composition.



Key:  $T_o$  = onset of polymerisation,  $T_{max}$  = maximum of enthalpy peak,  $T_f$  = final polymerisation temperature,  $\Delta H$  = polymerisation enthalpy, IL = 1-ethyl-3-methylimidazolium acetate, B = benzaldehyde, - = no reaction observed.

In all cases, the first exothermic reaction occurs at a higher temperature and the peak maxima are

shifted to higher temperatures for all the formulations containing adducts when compared with 1-ethyl-3-methylimidazolium acetate. Furthermore, the first peak appears to be better resolved and is completed before the second major thermal event occurs, implying that the adduct must undergo some rearrangement in order to initiate the reaction or the reaction proceeds *via* a different mechanism. The peak maxima for the major exotherm occur in similar temperature regimes irrespective of the adduct used, whereas those for the lower temperature peak are shifted to higher temperatures as the ionic liquid content in the adduct is reduced. This suggests that the first stage of the reaction which is sensitive to adduct concentration and further supports the hypothesis that the low temperature shoulder reaction is as a result of carbene formation; the residual ionic liquid in the adduct mixture will contribute towards the initiation of the curing reaction [23]. The latter may be the species responsible for the small shoulder peak on the first reaction (observed at 87 - 91 °C). From this preliminary study, the 1:1 adduct was selected for more detailed analysis and comparison with the corresponding ionic liquid, 1-ethyl-3-methylimidazolium acetate.

*Kinetics of initiation reaction.* The DSC data (various heating rates) for the formulation containing the difunctional epoxy (DGEBA) (5 g) and the 1-ethyl-3-methylimidazolium acetate-benzaldehyde (1:1 adduct) (0.25 g) are shown in Fig. 6, top. In this case the average functionality of the components in the formulation meant that it has the potential to form a three-dimensional network. All of the thermograms show similar features, with a lower temperature shoulder preceding a Gaussian shaped higher temperature exotherm. Plots of reaction conversion *versus* temperature (Fig. 6, bottom) show similarities between the higher heating rates, whereas the slowest rate (2 K/min) appears to display a more rapid conversion at up to 80%, but slower reaction thereafter.

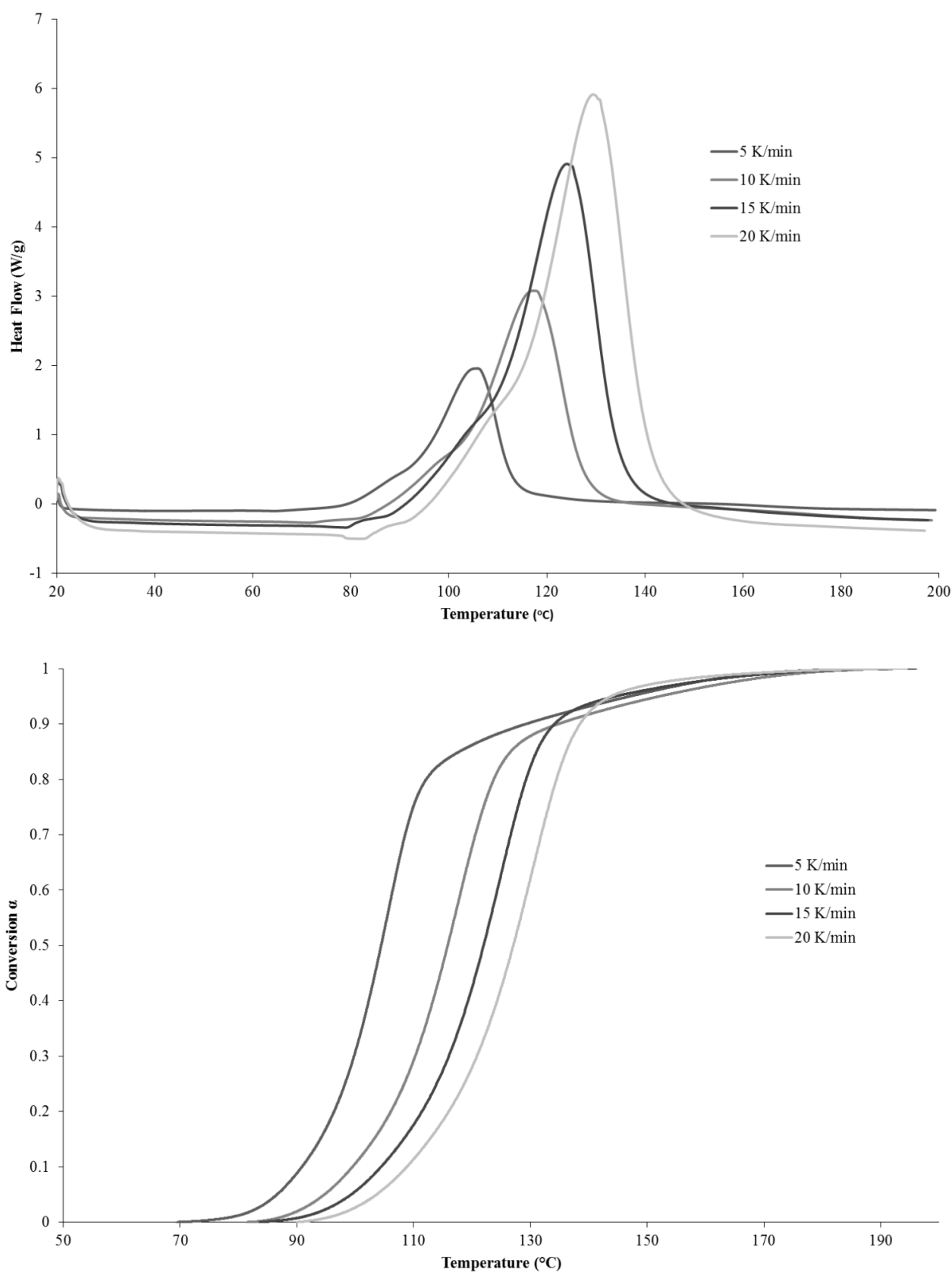


Figure 6. DSC data (top) and reaction conversion (bottom) as a function of temperature for freshly mixed formulations comprising DGEBA (5 g) and 1-ethyl-3-methylimidazolium acetate-benzaldehyde (1:1) adduct (0.25 g) at various heating rates.

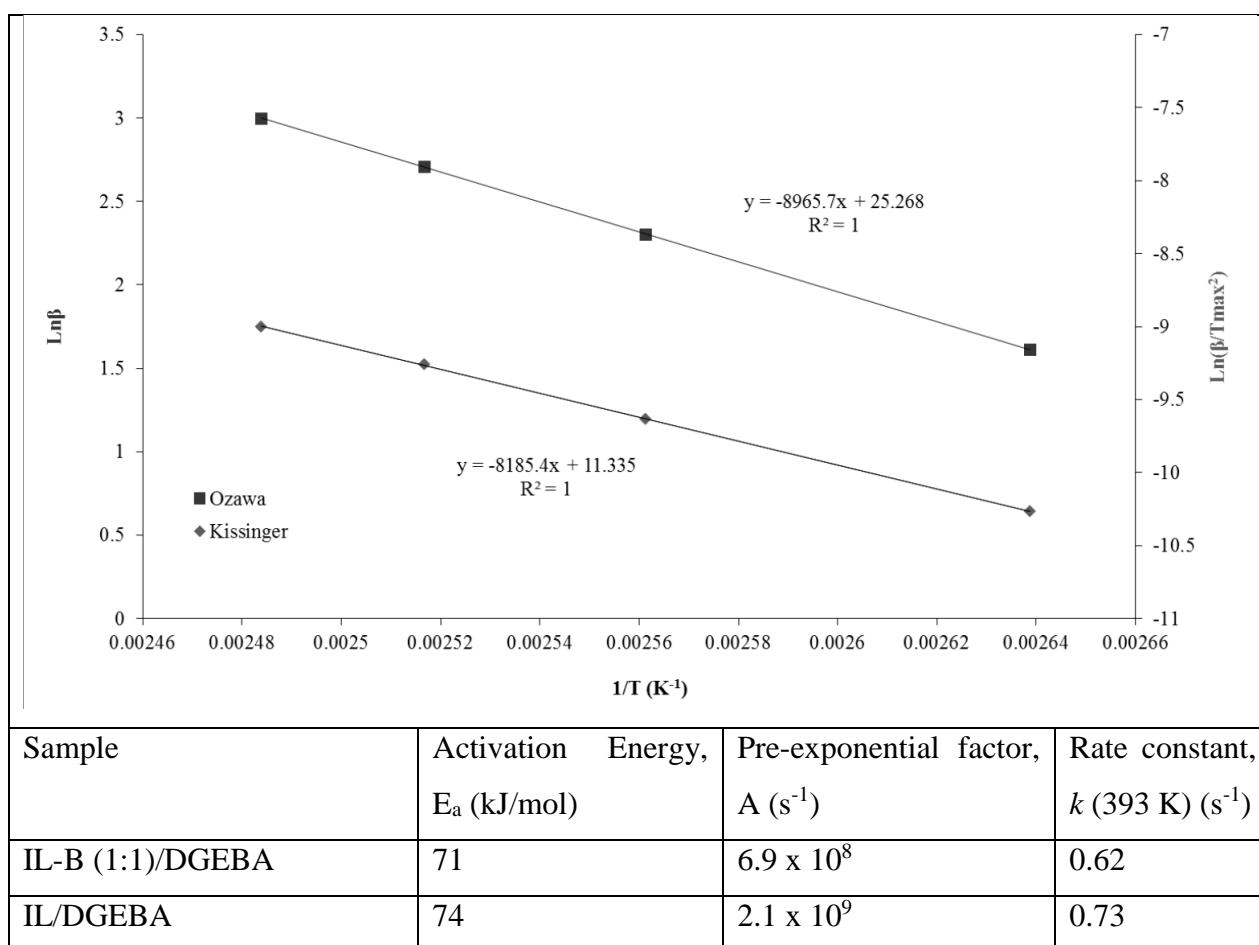
The kinetics of the initiation process for the adduct (IL-B) are compared with the pure ionic liquid (IL) using the Ozawa method [29], to determine the kinetic parameters of an epoxy curing reaction (eqn 1) and the regression coefficients ( $R^2$  values 1.00) show excellent linear fits to the DSC data (Table 6).

$$E_a = - \frac{R}{1.052} \cdot \frac{\ln \beta}{1/T_{max}} \quad (1)$$

where  $E_a$  = activation energy in kJ/mol.,  $R$  = universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $\beta$  = heating rate in K/min,  $T_{max}$  = temperature at peak maximum in DSC thermogram in °K.

From this analysis, the activation energies are calculated to be 71 kJ/mol. (IL-B) and 74 kJ/mol. (IL).

Table 6. Comparison of kinetic parameters for the cure of DGEBA (5 g) initiated with 1-ethyl-3-methylimidazolium acetate-benzaldehyde adduct (IL-B) (0.25 g) and 1-ethyl-3-methylimidazolium acetate (IL) (0.25 g)



In order to observe the effectiveness of the benzaldehyde on retarding the initiation reaction, the gel times determined for formulations comprising DGEBA and the 1-ethyl-3-methylimidazolium acetate-benzaldehyde (1:1) adduct. The samples were initially heated to 40 °C and held for 10 minutes (to avoid the sample heating too quickly) before being heated to 50 °C and the measurement started. In the presence of the pure ionic liquid, reaches gelation after 94 minutes, whereas the presence of the adduct increases this to 139-146 minutes (Fig. 7); no significant differences were observed between the gel times of the sequence of mixing.

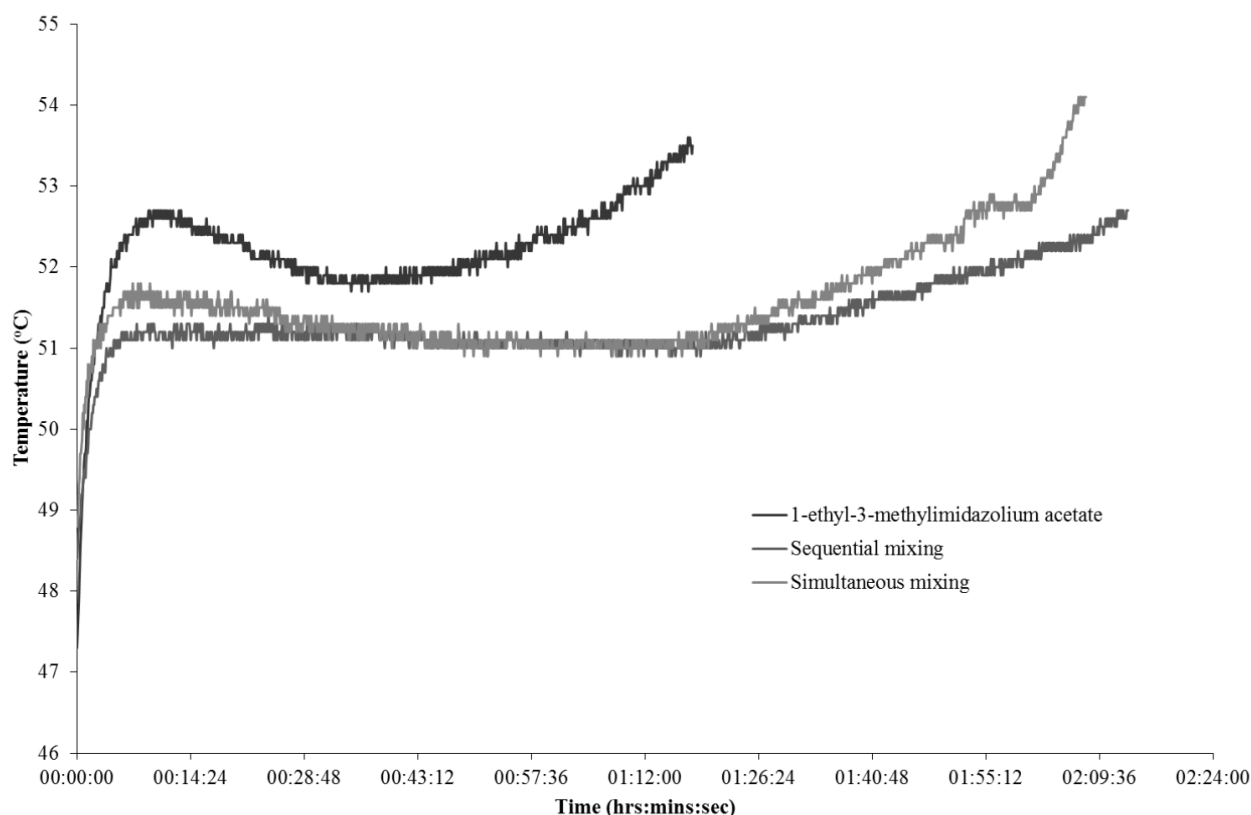


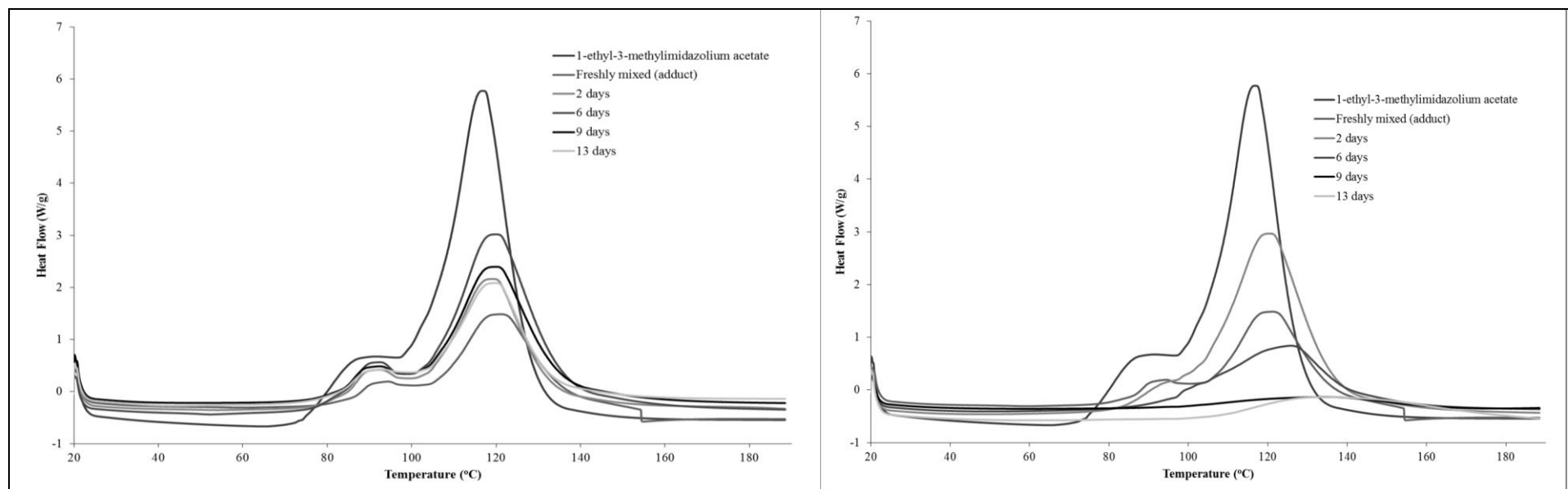
Figure 8. Comparison of thermal profiles resulting from gel time measurements for formulations comprising DGEBA (20 g) and either 1-ethyl-3-methylimidazolium acetate or 1-ethyl-3-methylimidazolium acetate-benzaldehyde (1:1) adduct (the latter as a function of mixing).

### Examining the effects of storage on the initiation of the adduct towards epoxy polymerization

The thermal behaviour of formulations comprising PGE and 1-ethyl-3-methylimidazolium acetate-benzaldehyde adduct (1:1 adduct) was examined to observe how these samples behaved during a period of storage at room temperature and sub-zero temperatures in the freezer (Table 7). The profiles of the thermograms for the frozen samples do not change considerably over the storage period (retaining two peaks), and the formulation retains a light yellow colour whilst at sub-zero

temperatures. In contrast, the 1:1 adduct/PGE sample quickly darkened to yield a viscous, dark red mixture as the onset temperature is increased and the exotherm is reduced. The lower temperature reaction is complete at room temperature, resulting in a single, broad exotherm at higher temperature. A very similar phenomenon was observed for both the 0.7:1 adduct/PGE mixture and the 0.5:1 adduct/PGE mixture at room temperature and at sub-zero temperatures (data not shown). The thermograms were deconvoluted using Grams<sup>TM</sup> peak fitting software (see Supplementary Data, Figs. S3-S12, and Table S1, S2) [30], from which it could be determined that as the storage time at ambient temperature increased, the percentage area assigned to the first process decreases. In contrast, when the peak fitting was applied to the samples stored in the freezer the areas of each peak remain broadly the same over the storage period. In contrast, in our previous manuscript [31], the study of the storage life of the PGE and 1-ethyl-3-methylimidazolium acetate (in the absence of benzaldehyde) revealed that the first peak in the DSC thermogram (90-99 °C) had been lost (and with it the capability to initiate the reaction) after only 10 days storage in the freezer.

Table 7. Dynamic DSC data (heat 1) for formulations comprising PGE (5 g) and 1-ethyl-3-methylimidazolium acetate-benzaldehyde (1:1) adduct (0.41 g) as a function of storage conditions (freezer stored samples, left; room temperature stored samples, right).



Storage time (d)	Freezer				Room Temperature			
	T <sub>o</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	ΔH (J/g)	T <sub>o</sub> (°C)	T <sub>max</sub> (°C)	T <sub>f</sub> (°C)	ΔH (J/g)
-	61	95, 121	154	294	61	95, 121	154	294
2	69	92, 119	184	392	68	121	181	537
6	63	92, 120	177	571	65	126	181	256
9	66	91, 120	174	425	80	134	171	58
13	66	92, 120	169	357	96	133	187	120



## CONCLUSIONS

An adduct formed from 1-ethyl-3-methylimidazolium acetate and benzaldehyde has been synthesised and identified using NMR spectroscopy. When equimolar amounts of the starting materials are used, the reaction mixture contains residual 1-ethyl-3-methylimidazolium acetate, whereas this is effectively consumed when a large excess of benzaldehyde is used. The reaction stoichiometry was not optimised beyond these two extremes (a 1:1 adduct and one in which the 1-ethyl-3-methylimidazolium acetate: benzaldehyde ratio was 0.1:1). Similar reactions employing 1-ethyl-3-methylimidazolium thiocyanate and benzaldehyde were unsuccessful, confirming that the basicity of the anion facilitates adduct formation *via* formation of a carbene prior to reaction with the benzaldehyde to generate the adduct. The order of mixing of the components of the blend does not influence the gelation behavior of the epoxy, but sequential mixing does appear to promote a higher glass transition temperature but a lower storage modulus. Furthermore, if the samples, regardless of the mixing methods, are cured up to a temperature of 160 °C this has an impact on the physical properties of the material and lowers the glass transition temperature.

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## REFERENCES

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1. Catalani, A.; Bonicelli, M. G. Kinetics of the curing reaction of a diglycidyl ether of bisphenol A with a modified polyamine. *Thermochim. Acta* 2005, 438, 126.
  2. Roşu, D.; Mustaţă, F.; Caşcaval, C.N. Investigation of the curing reactions of some multifunctional epoxy resins using differential scanning calorimetry. *Thermochim. Acta* 2001, 370, 105.
  3. Bao, X.; Cai, X. Synergistic effect of methyl phenyl silicone resin and DOPO on the flame retardancy of epoxy resins. *J. Thermal Anal. Calor.* 2014, 118, 369.

- 
4. Ham, Y.R.; Kim, S.H.; Shin, Y.J.; Lee, D. H.; Yang, M.; Min, J.H.; Shin, J.S. Effect of anhydride curing agents, imidazoles, and silver particle sizes on the electrical resistivity and thermal conductivity in the silver adhesives of LED devices. *J. Ind. Eng. Chem.* 2010, *16*, 556.
  5. Anand, M.; Srivastava, A.K. Synthesis of zinc-containing epoxy resin. *J. Appl. Polym. Sci.* 1994, *51*, 203.
  6. Radoman, T.S.; Džunuzović, J.V.; Jeremić, K.B.; Grgur, B.N.; Miličević, D.S.; Popović, I.G.; Džunuzović, E.S. Improvement of epoxy resin properties by incorporation of TiO<sub>2</sub> nanoparticles surface modified with gallic acid esters. *Mater. Des.* 2014, *62*, 158.
  7. Craver, C.; Carraher, C. *Applied Polymer Science: 21st Century* (Elsevier Science, 2000).
  8. Ghaemy, M.; Sadjady, S. Kinetic analysis of curing behavior of diglycidyl ether of bisphenol A with imidazoles using differential scanning calorimetry techniques. *J. Appl. Polym. Sci.* 2006, *100*, 2634-2639.
  9. Ito, M.; Hata, H.; Kamagata, K. Thermal properties of epoxy resin cured with imidazole. *J. Appl. Polym. Sci.* 1987, *33*, 1843.
  10. Barton, J.M.; Buist, G.J.; Hamerton, I.; Howlin, B.J.; Jones, J.R.; Liu, S. Preparation and characterization of imidazole–metal complexes and evaluation of cured epoxy networks. *J. Mater. Chem.* 1994, *4*, 379.
  11. Farkas, A.; Strohm, P.F. Imidazole catalysis in the curing of epoxy resins. *J. Appl. Polym. Sci.* 1968, *12*, 159.
  12. Fernández-Francos, X.; Cook, W.D.; Serra, À.; Ramis, X.; Liang, G.G.; Salla, J.M. *Polymer*, 2010, *51*, 26.
  13. Ooi, S.K.; Cook, W.D.; Simon, G.P.; Such, C.H. *Polymer*, 2000, *41*, 3639.
  14. Hamerton, I.; Howlin, B.J.; Jepson, P. Metals and coordination compounds as modifiers for epoxy resins. *Coord. Chem. Rev.* 2002, *224*, 67.
  15. Dupont, J.; Suarez, P.A.Z. Physico-chemical processes in imidazolium ionic liquids. *Phys. Chem., Chem. Phys.* 2006, *8*, 2441.
  16. Ghandi, K. A review of ionic liquids, their limits and applications. *Green Sust. Chem.* 2014, *4*, 44.
  17. Soares, B.G.; Livi, S.; Duchet-Rumeau, J.; Gerard, J.-F. Synthesis and characterization of epoxy/MCDEA networks modified with imidazolium-based ionic liquids. *Macromol. Mater. Eng.* 2011, *48*, 883.

- 
18. Kowalczyk, K.; Spychaj, T. Ionic liquids as convenient latent hardeners of epoxy resins. *Polimery* 2003, 48, 883.
  19. Rahmathullah, M.A.M.; Jeyarajasingam, A.; Merritt, B.; Van Landingham, M.; McKnight, S.H.; Palmese, G.R. Room temperature ionic liquids as thermally latent initiators for polymerization of epoxy resins. *Macromolecules*, 2009, 42, 3219.
  20. Maka, H.; Spychaj, T.; Pilawka, R. Epoxy resin/ionic liquid systems: the influence of imidazolium cation size and anion type on reactivity and thermomechanical properties. *Ind. Eng. Chem. Res.* 2012, 51, 5197.
  21. <http://www.gelinstrumente.ch/en/prодукte/conductivity-or-viscosity/gelnorm-rvn> (accessed December 2013).
  22. Rodriguez, H.; Gurau, G.; Holbrey, J. D.; Rogers, R. D. Reaction of elemental chalcogens with imidazolium acetates to yield imidazole-2-chalcogenones: direct evidence for ionic liquids as proto-carbenes. *Chem. Commun.* 2011, 47, 3222.
  23. Binks, F. C.; Cavalli, G.; Henningsen, M.; Howlin, B. J.; Hamerton, I. Investigating the mechanism through which ionic liquids initiate the polymerisation of epoxy resins. *Polymer*, 2018, 139, 163.
  24. Binks, F. C.; Cavalli, G.; Henningsen, M.; Howlin, B. J.; Hamerton, I. Examining the kinetics of the thermal polymerisation behaviour of epoxy resins initiated with a series of 1-ethyl-3-methylimidazolium based ionic liquids. *Thermochim. Acta*, 2018, 663, 19.
  25. Handy, S. T.; Okello, M. The 2-position of imidazolium ionic liquids: Substitution and exchange. *J. Org. Chem.* 2005, 70, 1915.
  26. Rosa, J. N.; Afonso, C. A. M.; Santos, A. G. Ionic liquids as a recyclable reaction medium for the Baylis–Hillman reaction. *Tetrahedron* 2001, 57, 4189.
  27. Aggarwal, V. K.; Emme, I.; Mereu, A. Unexpected side reactions of imidazolium-based ionic liquids in the base-catalysed Baylis–Hillman reaction. *Chem. Commun.* 2002, 1612.
  28. Kalsi, P. S. *Spectroscopy of Organic Compounds*, 6<sup>th</sup> Edition (New Delhi: New Age International Publishers Limited, 2004) pp. 216.
  29. Kissinger, H.E. Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand.* 1956, 57, 217.
  30. <http://www.asdi.com/products/spectroscopy-software/grams-suite> (accessed March 2012).
  31. Binks, F. C.; Cavalli, G.; Henningsen, M.; Howlin, B. J.; Hamerton, I., Examining the effects of storage on the initiation behaviour of ionic liquids towards the cure of epoxy resins, *Reactive and Functional Polymers*, 2018, 133, doi: 10.1016/j.reactfuncpolym.2018.09.017.